WATER, CLAY AND ROCK SOUNDNESS[1, 2]

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ABSTRACT

The nature of water and clay in carbonate rocks is currently being investigated at Rensselaer Polytechnic Institute by various thermal and sorption techniques.

Two basic concepts led to the present research. (1) To explain the expansion and contraction on wetting and drying of some unsound argillaceous carbonate rocks, it was postulated that the pore space around each clay particle is such that when water is sorbed by the clay, force is exerted against the pore walls. (2) The clays in expansive rocks are rejected from the growing dolomite crystals during their growth, and form a more or less connected network, thereby becoming "wettable," or available to water.

New quantitative cold differential-thermal-analysis (electrocalorimetric) equipment was designed and constructed to check the "limited space" and "wettable clay" concepts and to determine the thermal nature of the transition of water to ice in rocks. This DTA equipment can detect the release of heat in freezing of less than 0.001 per cent water in a rock.

Twenty-three rock cores (nine sound and fourteen unsound) and 4 procelain cylinders for standards were studied. In the nine sound rocks and in all the procelain cylinders, the rapid freezing of from 50 to 100 per cent of the water was readily detectable after 7 to 10° C of supercooling. No further freezing could be detected to −20° C. However, in eleven of the fourteen unsound rocks, no freezing was detected to as low as −40° C; in the other three, less than 50 per cent of the water froze.

As a check of the DTA measurements, adsorption isotherms were determined for all materials. Calculations of theoretical freezing points for sorbed water again demonstrated that the least sound rocks had the most nonfreezable water.

"Frost" sensitivity in these carbonate rocks is, therefore, probably not the result of the force of expansion of water to ice. The disruptive force is believed to result from expansion of sorbed, ordered water on clay surfaces.

The relationship between the unfilled rock pores after 24-hour water saturation and the water sorbed at 85 per cent humidity at 30° C (i.e., the theoretical nonfreezable water delineates the sound and unsound carbonate rocks.

INTRODUCTION

The purpose of this discussion is to talk about water—an odd kind of water—and about clays—very common clays— and how they probably conspire to destroy carbonate rocks.

For many years there have been two major approaches to the study of frost deterioration in rocks. Engineers, largely in the Portland Cement Association, led by such people as Powers and Verbeck, have stressed the importance of pore characteristics. Their theories, based on work with portland cement, were brilliantly conceived and seemed to have some applicability to aggregates.

The other approach has been largely geologically oriented and has been propounded by such workers as Lemish, the Mathers, and Mielenz. They said, in effect, that pore characteristics were certainly important, but mineralogy and petrography were also apparently critical. It has long been obvious to both groups, for instance, that clays have an influence on rock soundness. As an ex-

[1]Contribution 65–10, Dept. of Geology, Rensselaer Polytechnic Institute. Based on research by James R. Dunn and Peter P. Hudec.

[2]The experimental data which are summarized in this paper are a portion of the results obtained under a research contract between Rensselaer Polytechnic Institute and the New York State Department of Public Works in cooperation with the U. S. Department of Commerce, Bureau of Public Roads. The views that are expressed in the paper are those of the authors and not necessarily endorsed by the New York State Department of Public Works. The complete results of this research have been published by the NYSDPW as Research Reports 65–1 and 65–5. Extensive expansions of the concepts expressed herein will appear in other publications later in 1966.

ample, shales are recognized as the least sound rocks, so it was clear, therefore, that somehow dolomite and clay together must be a bad combination of minerals, leading to unsoundness.

While we agree that studies of pore size, mineralogy, and petrography have been productive paths to follow, we have added cold differential thermal analysis and thermodynamic calculations pased largely on adsorption isotherms. This multiple approach sheds light on areas formerly either not understood or poorly understood.

A basic assumption, which seems irrefutable, is made by both groups of researchers: that frost deterioration of rock is the result of the 9 per cent expansion that occurs when water changes to ice. The breakdown process is similar to that occurring when water freezes in a soda bottle. We found, however, that in many so-called frost-sensitive carbonate rocks, ice very probably cannot form at any temperature. This will be shown to be consistent with petrography, clay mineralogy, quantitative calorimetric measurements, and thermo-dynamic calculations. Finally this will be integrated with some observations on pore characteristics and a simple method will be suggested by which frost-sensitive rocks can be distinguished from sound carbonate rocks in the laboratory.

SPECULATIONS LEADING TO ADSORPTION AND DTA STUDIES

The Problem

Sound rocks in the clay-carbonate system are generally the calcitic limestones, the pure dolomites, the dolomitic limestones and some argillaceous limestones. Conversely, nearly all shales, shaly limestones, shaly dolomites, or dolomitic rocks containing disseminated argillaceous materials are unsound.

Note that the common denominator for unsoundness is clay in one form or another. But clay disseminated in calcite does not always seem to be a problem, even when present to the extent of 30 per cent or more. A good example of such clay in sound limestone is the New Scotland Formation of the Helderbergian Group in the Hudson Valley. It contains up to 40 percent clay, rarely less than 10 per cent judging from hundreds of chemical analyses (Johnsen, 1958, and cement and stone company files), and yet is fundamentally a sound rock which passes New York State Department of Public Works (N.Y.S.D.P.W.) tests for soundness and has never been known to fail in use (Dunn and Rickard, 1961).

WET-DRY SENSITIVITY

That some of the unsound rocks of New York are sensitive to simple wetting and drying was discovered somewhat accidentally. At Rensselaer, we had been conducting research, sponsored by the New York State Department of Public Works in cooperation with the U. S. Bureau of Public Roads, on carbonate rocks of western New York. In this research the physical and chemical characteristics of 80 typical lithologies were determined and correlated (Dunn, 1963). In all, 31 kinds of determinations were made, including various tests for soundness, porosity, specific gravities, chemical analyses, X-ray mineralogy, petrographic analysis, normative mineralogies by computer, compressional and shear-wave velocities, Poisson's ratios, and thermal expansion from $-60°$ C to $+20°$ C for three orientations.

The determination of so many characteristics for 80 samples would seem to be a relatively thorough piece of research, but the experiment which gave the original impetus to the work on which I am reporting did not result from research which was planned. For several months, without my knowledge, a graduate student (Mohammed, 1963) had been periodically soaking certain of our carbonate rocks in tap water for 12 or more hours at ambient conditions and drying them at 110° C. Of 10 groups of samples, 3 were showing marked deterioration in the form of fracturing. Figures 1 and 2 are photographs of two typical argil-

laceous dolomites which had deteriorated by wetting and drying. The specimen of figure 1 is from the Gasport Member of the Lockport Formation; the sample in figure 2 from the Pamelia Formation. It is estimated, on the basis of later tests, that probably most of the unsound carbonate rocks tested would so deteriorate. Typical shales from the Rochester, Esopus, Normanskill, and Catskill Formations also deteriorate, generally in from one to five cycles.

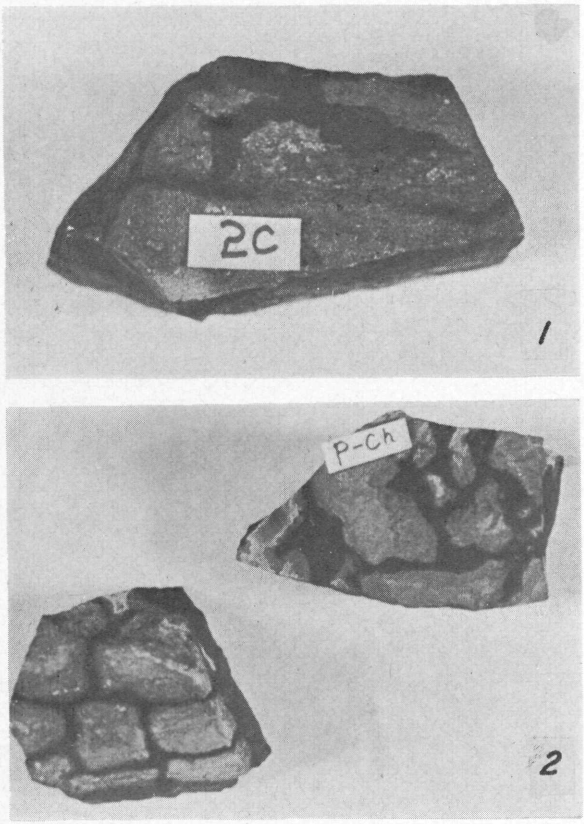
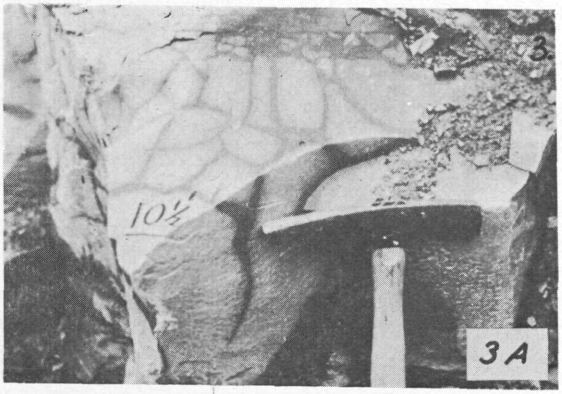


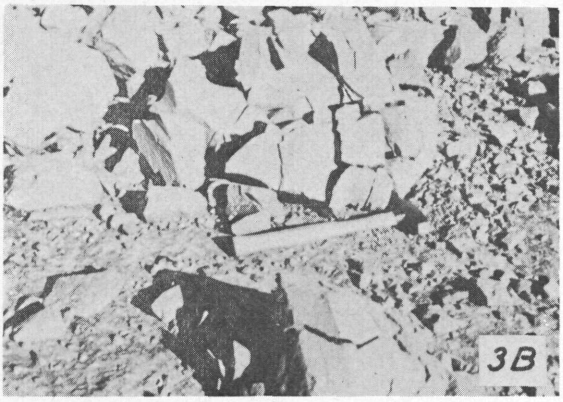
FIGURE 1. Specimen, Gasport Member of Lockport Formation, Lockport, N. Y., after wet-dry deterioration.
FIGURE 2. Specimen, Pamelia Formation, Chazy, N. Y., after wet-dry deterioration.

Figure 3 shows a layer of Pamelia Formation at La Fargeville, New York, after one winter season. The sample in figure 4 is some Gasport rock after a few seasons (less than five years). One is led to speculate that the deterioration in the field may be by wetting and drying, not frost action. The simplest explanation for such wet-dry deterioration is that clays in small spaces either adsorb or absorb water and exert a force against the pore walls.

Similar deterioration has been described before by Rhodes and Mielenz (1946) and by Thomas (1938). They correlated wet-dry deterioration with the content of montmorillonite or other expansive clays. However, in rocks of Ordovician, Silurian, and Devonian ages, such clays are not generally found. X-ray studies of over 80 carbonates (Dunn, 1963; Kaufman, 1963) disclosed only well crystallized

illite, kaolinite and chlorite, just as other workers, such as Lemish (Lemish, Rush and Hiltrop, 1958), had discovered. The most likely explanation seems to be that ordered water on clay surfaces is capable of exerting great force.





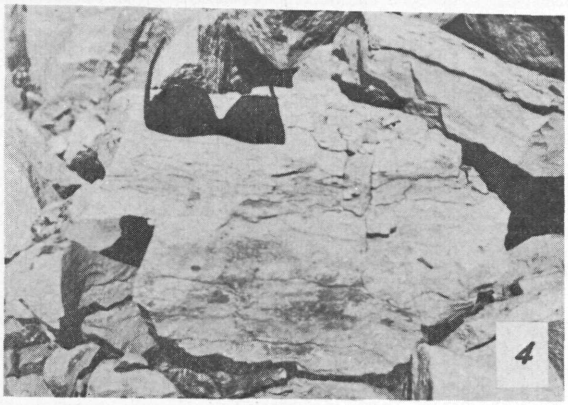


FIGURE 3. Field deterioration of Pamelia Formation at LaFargeville, N. Y. (A), and Chazy, N. Y. (B).

FIGURE 4. Field deterioration of Gasport Member at Lockport, N. Y.

The observation of deterioration due to wetting and drying led to the "limited space concept:" *The pore space around each clay particle in expansive carbonate rocks is such that when water is sorbed by the clay, force is exerted against the pore walls.* With too little space, water could not be taken in; with too much space, the adsorbed water could not exert effective pressure. The repeated stressing of the rock through wetting and drying can exceed the tensile strength of the rock.

The Rejection Texture

The above hypothesis did not say *why* the clays should have just that much space around them in carbonate rocks. The key to the problem seemed, somehow, to be in the textural differences between argillaceous limestones and argillaceous dolomites. Fig. 5 compares typical recrystallization textures for some argillaceous limestones and argillaceous dolomites. Two things are immediately obvious. In these limestones, the clay is discontinuous and intimately related

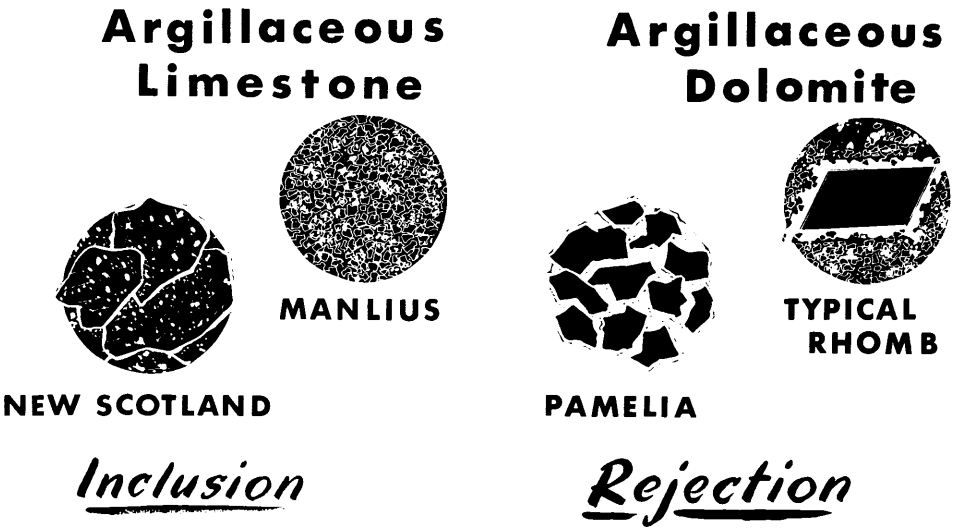


FIGURE 5. Clay-carbonate textures.

with the calcite, either within single crystals or intimately intermixed. Such calcite is usually cloudy because of these impurities. Dolomite, however, tends to be clear, and any clay appears to be interstitial (for good examples see Hadley, 1964). Clays tend to be rejected from growing dolomite crystals and made relatively continuous. In a sense, by becoming more continuous, the clays in dolomites become more like the clays in shales, the most unsound of the common sedimentary rocks.

Wettable-Clay Concept

Dolomite, thus, may be a factor in making the clays more available to water by making them more continuous. Loughlin (1923) indicated the importance of clays in rock soundness, and stressed that they must not only be present, but must be *available to water.*

If the wettable clays are dolomite-associated, then if the normative clay content from chemical analysis is corrected for per cent of dolomite, the per cent of water absorbed should be proportionate to this so-called wettable clay. Samples of the 18 most frost-sensitive of over 80 rocks studied previously were taken and for each, a plot of wettable clay was made against water absorption in 24 hours

(Dunn, 1964) (Recent work correlating "available clay" and water absorption indicates that the correlation may be valid also for many sound rocks.). Some correlation was evident, but there were erratic points. Some erratic points are not too strange, inasmuch as (1) the individual clay minerals were not identified (2) the normative calculations for clay were not too satisfactory, and (3) some of the porosity was almost certainly not associated with clays.

However, a relationship seemed to exist. This led to the wettable- clay concepts, which is as follows: *Clays are rejected by dolomite when it replaces calcite in argillaceous limestones. The rejected clay tends to form a continuous network and thereby becomes wettable.* It was postulated that each clay particle had adhering to it as much water as it could hold under the lithic pressures existing at the last period of recrystallization. Possibly the clay particles, if wet at the temperatures of this last recrystallization, are capable of exerting a pressure approximately equal to the original lithic pressures.

CHARACTERISTICS OF A CLAY-WATER SYSTEM

If the above speculations are true, we are dealing with a clay-water system, and much is known about such systems. More important, many things can be measured.

For instance, the negative charges on clay surfaces have a strong ordering effect on the highly polar water molecules. The hydrogen side of the water molecule tends to attach strongly to the clay surface, apparently with a force that may be stronger than the bonding in ice.

It is known that much of such water is non-freezable, has low vapor pressure, and low entropy—so low, in fact, that it has been demonstrated thermodynamically that, for the first few water layers, heat would probably have to be added before ice could form. Such water should have high shear strength, be rigid, and be capable of exerting force. Clay mineralogists are in general agreement about these characteristics (Anderson and Low, 1958; Barshad, 1959; Kalaian, J. H., 1960; Low, 1959; Martin, 1959).

MEASUREMENTS ON THE NATURE OF ICE AND WATER IN CARBONATE ROCKS

Based on research concerned with freezing of clays, it is known that if the water in unsound carbonate rocks is largely clay-associated, much of it must be non-freezable. In addition, the water should be adsorbed rapidly at various humidities. Also, by calculation from adsorption characteristics, the theoretical quantities of freezable water can be determined. The two primary tools by which it was decided to study these characteristics were quantitative cold DTA, or electrocalorimetry (Hudec, Dunn, and Schwarzer, 1964), and adsorption at varying humidities at constant temperature, that is, adsorption isotherms.

QUANTITATIVE COLD DTA

There was no previous work from which to draw to make cold DTA (differential thermal analysis), that is, DTA which could detect the heat liberated during the freezing of water. However, such a system is basically simple and must consist of a recording system, a differential system, and an electro-calorimetric system.

Nature of the Equipment

Figure 6 is a diagram of the major equipment used. The central system, the differential thermal analysis system (DTA), has a cylindrical standard of portland cement, barite, and calcite, that is 2 inches long by ¾ inch diameter in a standard cell, and the study specimen of the same dimensions in another cell. Both cells are cooled simultaneously, at a rate of approximately 10° C per hour, in a refrigerated glycol bath, which pumps glycol through copper tubes wound

around the differential unit. When freezing occurs, the heat liberated is detected by four thermocouples, two in the "standard" cell, two in the "unknown" cell.

The system is made quantitative through the electrical calorimetric system. Voltage is supplied by a 12-volt battery for a measured interval of time to a resistance wire encased in the standard. A known voltage through a known resistance for a known period of time produces a given heat output.

All heat differentials, amplified in a potentiometric micro-millivolt amplifier, are recorded in the recording system as temperature differences. In addition, a thermister probe constantly measures and records the temperature of the aluminum block.

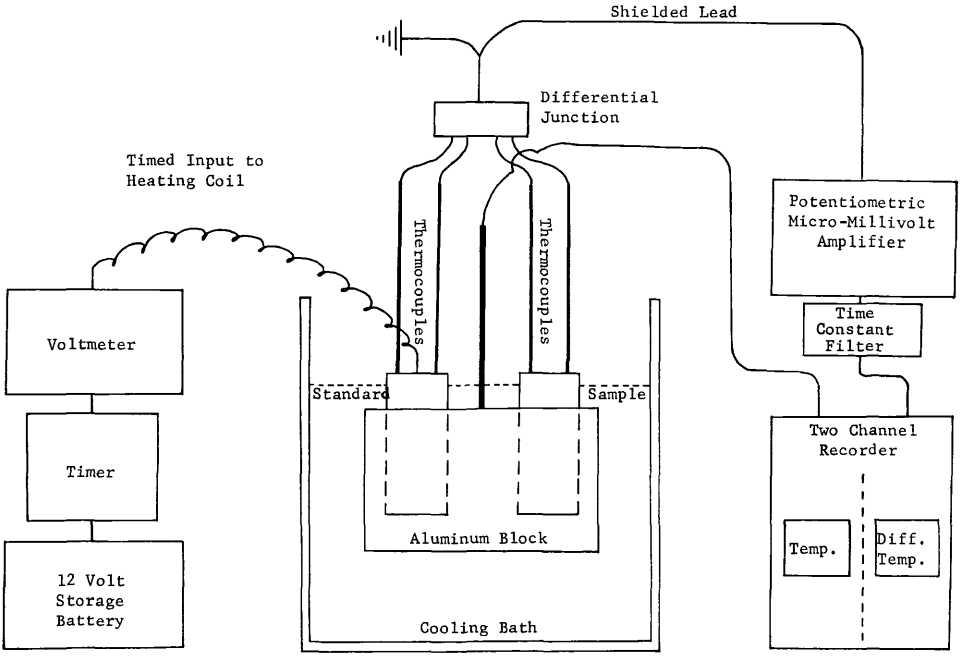


FIGURE 6. Schematic diagram of quantitative cold DTA equipment.

Figure 7 shows half of the differential cell. As heat is liberated from the ¾-inch rock cylinder when water freezes, or from the calorimetric standard when electrical current is passed through, the temperature of the surrounding copper jacket is raised and is picked up by the thermocouples set in the copper tube. The lucite cylinder acts as an insulating sheath, which allows the heat to build up sufficiently so that it can be detected. The purpose of the aluminum casing is to spread the cooling effects evenly between the two differential cells, because any slight difference in currents in the cooling solution will radically alter the recorded traces. (For complete details of construction and calibration, see Dunn and Hudec, 1965a.)

Accuracy of the Equipment

At the time most of the measurements referred to in this presentation were made, the accuracy of heat measurements was to ±0.9 per cent in intermediate- to high-heat-output ranges; the temperature differences which could be detected were 0.009° C or approximately 0.2 calories heat difference. Freezing was detected readily in rocks containing as little as 0.01 per cent water. (Recent im-

provements in the cooling system have now given us enough sensitivity to detect the freezing of 0.001 per cent water in a rock.

Samples Studied

Nine sound and 14 unsound typical non-shaly carbonate rocks from New York State quarries, and 5 porous procelain cylinders with capillary radii of 2.1, 1.5, 0.7, 0.42 and 0.22 microns were studied with the DTA. Table 1 summarizes

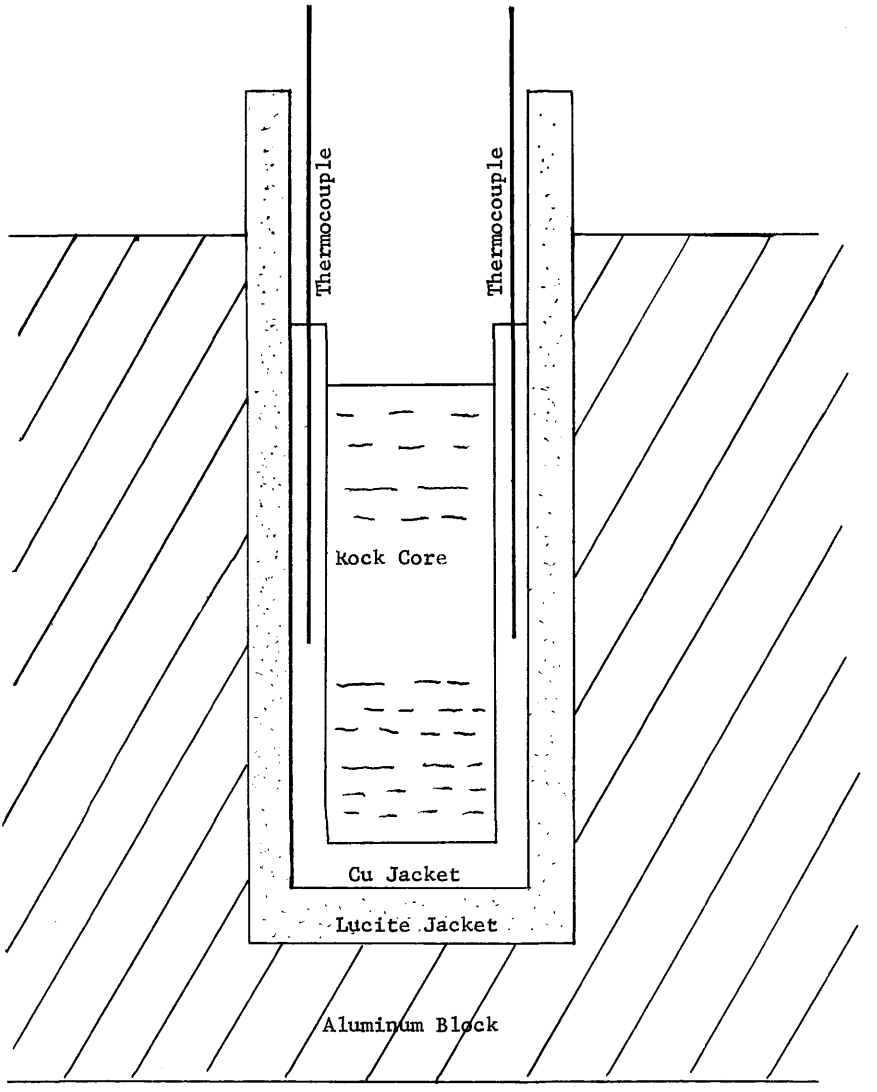


FIGURE 7. Cross section of the half of the DTA cell that contains the sample. (Not to scale.)

the samples studied. For most of the rock samples, some 30 characteristics had been measured in previous research so that their basic nature was well understood. The rocks chosen were non-shaly and none was obviously unsound. They were typical limestones and dolomites, argillaceous and non-argillaceous, sound and

unsound on the magnesium-sulfate, sodium-sulfate, and 25-cycle freeze-thaw test of the New York State Department of Public Works (Dunn and Hudec, 1956b; Hudec, 1965). Freeze-thaw unsoundness is here defined as a loss of over 10 per cent in the freeze-thaw test in 10 per cent NcCl solution. Cooling in this test is to about −20° C and warming is to about +20° C, one cycle taking one day.

To determine the ability of the N.Y.S.D.P.W. freeze-thaw test to predict soundness, a systematic study was undertaken by a graduate student at Rensselaer in the summer of 1964, to determine the relationship between the freeze-thaw test

TABLE 1

Sample descriptions

Sample no.	Formation	Member	Location (in N. Y. state)
42	Onondaga	Nedrow	Jamesville (Syracuse)
EA1	Manlius	Jamesville	Perryville
42 JO	Manlius	Jamesville	Jamesville
26 J	Manlius	Jamesville	Oriskany Falls
CR	Manlius	Clark Res.	Perryville
R-1-1	Manlius	Elmwood C	Perryville
24 EC	Manlius	Elmwood C	Paris
26EA	Manlius	Elmwood A	Oriskany Falls
OD	Manlius	Thacher	Syracuse
RA	Manlius	Thacher	Syracuse
K-2	Cobleskill	————	Phelps
8b	Lockport	Oak Orchard	Sodas
2e	Lockport	Goat Island	Lockport
6b	Lockport	Penfield	Gates
7a	Lockport	Penfield	Penfield
9	Lockport	Penfield	
C-1-1	Lockport	Gasport	Lockport
2c	Lockport	Gasport	Lockport
3b	Lockport	Gasport	Gasport
4b	Lockport	Gasport	Glarendon
5b	Lockport	Brockport	Brockport
5a	Lockport	Brockport	Brockport
P-B-2	Pamelia-Lowville	————	Lowville
P-B-1	Pamelia-Lowville	————	Lowville
P-A-1	Pamelia-Lowville	————	Lowville
LO	Pamelia-Lowville	————	Lowville
M	Pamelia	————	LaFargeville

and deterioration by natural weathering. He found that natural deterioration of 31 separate unsound layers of carbonate rocks correlated significantly with results of the test; that is, a high test loss correlated with rapid deterioration of the rock on a quarry floor or in quarry walls. The N.Y.S.D.P.W. freeze-thaw test is, therefore, a useful reference for research conducted to determine the nature of soundness and unsoundness in carbonate rocks.

Samples for study in the DTA unit are 2 x ¾-inch cores which were cut from slabs sawed parallel to the bedding planes. Several cores were cut from each slab and subjected to various tests, including a freeze-thaw test to check previous tests on soundness.

Typical Curves

Figure 8 shows typical differential temperature traces obtained on the DTA recorder. Trace A is the most common type recorded. It is typical of all sound rocks and of all short-duration (less than 30 seconds) heat-output curves resulting when EMF (electro-motive force) is fed through the electrical standard.

The curve shows, first, equilibrium cooling, that is, no temperature difference between the cells (1), followed by sudden heating (2), at -2 to $-7°$ C for rock samples. The sharp peak (3) indicates sudden cessation of heat output. The height of the peak is directly proportional to the heat output, as is the area under the curve. The cooling curve (4) is exponential in shape (plotting as a straight line on semi-log paper) and indicates that no more heat is being added. With further cooling to $-20°$ C, no additional heat release was detected. A thermal

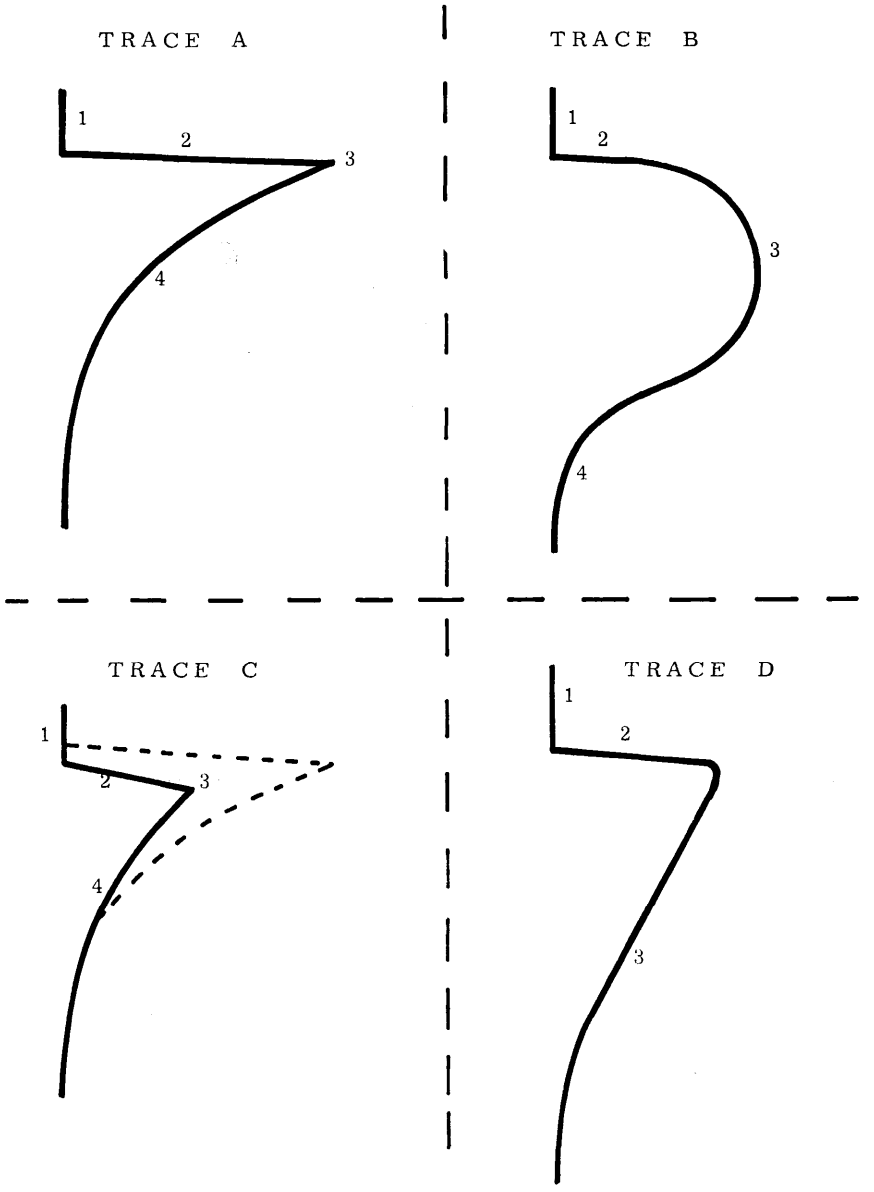


FIGURE 8 FREEZING CURVES

trace of this type should be typical of any sound rock in which the heat liberated when water freezes is less than the system can absorb; i.e., the specific heat of rock plus copper, times the degree of supercooling prior to freezing, is equal to more calories than are liberated when the water freezes.

The interpretation for the freezing behavior of water in these rocks is that first the rock is supercooled to between −2° C and −7° C, whereupon freezing begins. All water which is freezable in the range 0° C to −20° C is frozen essentially instantaneously, liberating heat, and then cooling continues until the standard and the differential cell are at the same temperature, and they then cool in equilibrium to −20° C when the run is stopped. In most cases no additional freezing was detected after this initial freezing pulse.

Trace B is typical of water freezing in a saturated porous porcelain cylinder. The amount of heat liberated by the large quantity of freezing water (4–5 grams or 20 to 30 per cent H_2O) could not be readily absorbed by the system consisting of copper plus specimen at the temperature of initial freezing. The specific heat of this system is about 24 calories/1° C. Thus at −10° C, for instance, it can readily absorb 10 x 24, or 240 calories before the heat liberated raises the temperature to 0° C. In the case of the porcelain cylinders, the freezing of water liberated is more than dT_f x Cp system calories, where dT_f is the amount of supercooling in degrees centigrade and Cp system is the approximate heat capacity of the copper plus the rock core (24 calories).

The interpretation of the trace is that, following supercooling to −7 to −9° C, sudden freezing occurs. The curve breaks when the system cannot quickly absorb any more heat. The calorie output indicated by the length of the straight part of the trace (2) shows that the heat liberated is nearly equal to the specific heat of the system times the number of degrees of undercooling. This shows that the temperature of the system has reached nearly 0° C at the point at which the curve breaks. Now the curve (3) is a compromise between heat added as more water freezes and the slow cooling of the system. All water is soon frozen and, at part (4) of the curve, the cooling is again exponential. No further freezing was detected.

In the five porcelain cylinders tested, the heats liberated were in excess of 300 calories, and over 90 per cent of the contained water froze.

Trace C is the typical DTA curve made by freezing a 10 per cent NaCl-water solution (used in the N.Y.S.D.P.W. freeze-thaw test) in rock cores, compared with a curve formed by freezing pure water (the ghost curve). One frost-sensitive and 3 sound rocks have been run in the NaCl solution to date. This curve is characterized by: (a) a depression in the initial freezing point by 3 to 4° C to a temperature of −7° C or −12° C, (b) a reduction of 20 to 60 per cent in the quantity of freezeable water, as indicated by the shorter height of the peak, and (c) a slower rate of freezing, as indicated by the less abrupt break (2) from the equilibrium cooling at (1). It might seem paradoxical that freezing with a 10 per cent NaCl solution in rock increases the severity of freezing and thawing by a factor of more than 10 over the severity of freezing and thawing of pure water, but less ice is formed and it is formed more slowly.

Trace D is an abnormal sort of curve found in 3 frost-sensitive rocks and in 3 portland-cement pastes. Equilibrium cooling was followed by sudden freezing of some of the water. Then apparently incremental quantities of water continued to freeze and normal exponential cooling was not observed. The quantity of water in the rock was such that all of it could have frozen suddenly, considering the heat capacity of the system and the degree of supercooling.

SUMMARY OF DTA RESEARCH RESULTS

The research results from DTA work can be summarized as follows. In all nine sound rocks, freezing occurred suddenly between −2° C and −7° C. No further freezing was detected to −20° C. *No freezing whatever* could be detected

to −20° C for 8 of 14 frost-sensitive rocks. Water freezing could not even be detected in 5 of these frost-sensitive cores cooled to −37 to −40° C—the only samples so tested. For the three frost-sensitive rocks in which water froze before −20° C, the heat loss indicated that less than 50 per cent of the total water froze. In the sound rocks and in the porcelain cylinders, however, from 50 per cent to 100 per cent of the contained water froze.

The paradox is obvious. Eight out of 14, or nearly 80 per cent of the least sound rocks apparently had no water which was freezable at temperatures to −20° C or lower, i.e., the frost sensitivity would seem to be *inversely proportional* to the quantity of ice that forms. These observations are in radical conflict with most concepts of frost deterioration.

As noted before, the addition of sodium chloride serves to reduce even further the quantity of ice that forms, and to make the formation of ice at these temperatures even less likely. (Incidentally, of course, this does not imply that if ice formed in the unsound rocks they would necessarily become more sound!)

ADSORPTION ISOTHERMS

To check the DTA data, adsorption isotherms were run at +30° C, and calculations of freezing temperatures for the contained water were made. The method of determining adsorption isotherms and the calculations of freezing points from vapor pressures will not be elaborated here, because the techniques have been well known for many years (Feldman and Sereda, 1961). Basically, adsorption isotherms are curves showing the quantity of water adsorbed at different vapor pressures at a given temperature. Vapor pressure is easily controlled by using saturated solutions of various salts. The freezing temperatures can be calculated because partial water pressure and freezing points are interdependent, according to the following equation:

$$\frac{\ln h_{30}}{\ln h_t} = \frac{\sigma\, 30}{\sigma\, t} \cdot \frac{T}{303} \cdot \frac{v_{30}}{v_t}$$

Where:
- h_{30} = relative vapor pressure at 30° C
- h_t = relative vapor pressure at temperature T
- $\sigma\, 30$ = surface tension of water at 30° C
- $\sigma\, t$ = surface tension of water at T
- T = temperature of ice, °K
- v_{30} = volume of water at temperature 30° C
- v_t = volume of water at temperature T

(Note: This equation is valid for salt solutions, but gives only approximate results for adsorbed water.)

The adsorption isotherms for frost-sensitive rocks had a characteristic shape, because the rocks adsorbed much water at low relative humidities. In addition, calculations of freezing temperatures from the isotherms indicated that the water in frost-sensitive rocks was from 45 to 80 per cent non-freezable, even to −20° C. The percent of non-freezable water in the sound rocks and porcelain cylinders was from about 55 per cent to zero—that is, from 45 to 100 per cent of the water should freeze according to calculations from partial-pressure data.

RELATIONSHIP BETWEEN DEGREE OF SATURATION AND FREEZABLE WATER

At first thought, the probability that frost-sensitive rocks contain less freezable water than sound rocks seems to be in major conflict with much previous work on pore characteristics and saturation. However, by making one more set of measurements on 22 of the cores studied, it has been possible to show that this work actually is somewhat complementary to previous work and some of the inconsistency vanishes.

It was decided to determine the degree of saturation reached by the samples after soaking for 24 hours in water at ambient conditions. The techniques of measurements made are fairly standard, consisting first of determining the 24-hour water saturation by immersion, followed by vacuum-saturation of the specimens by first evacuating them and then placing them in water without removing the vacuum. By substracting the weight after 24-hour water soaking from the weight after vacuum absorption, it is possible to get an indication of the amount of air

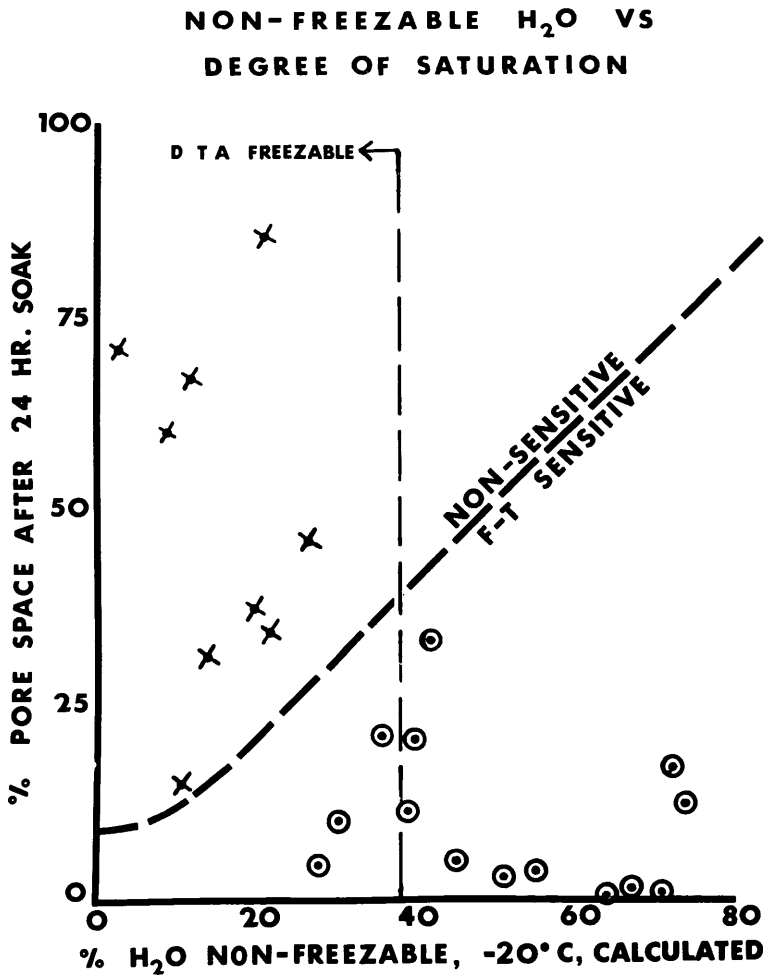


FIGURE 9. Non-freezable H_2O vs. degree of saturation.

space which remains after 24-hour saturation. A rock with 8.3 per cent or less void space after 24-hour saturation is considered to be "critically saturated" (Verbeck and Landgren, 1960) and potentially deleterious in line with previous research work by others; i.e., if water froze, there would not be enough space in the rock to take up the expansion and hence pressure would be exerted by the ice.

In figure 9 this void space is plotted against the per cent of non-freezable water at $-20°$ C, as calculated from adsorption isotherms. In a sense, previous research has been concentrated on the ordinate, which relates deterioration to ice, while

this work is mainly concerned with the abscissa, which relates deterioration to water. Frost-sensitive rocks are represented by circled dots, and sound rocks by X's. As can be seen, a line can be drawn which separates the frost-sensitive rocks from the sound rocks. The dashed vertical line separates the rocks which contained measurable freezable water (by DTA) from those which did not. Note the position of the three frost-sensitive rocks to the left of the dashed vertical line.

This single diagram summarizes our research showing the relationship between the theoretical content of freezable water and that which we could measure. Further, it relates this work to previous work and to frost-sensitivity in general.

Although this research was on carbonate rocks (and porous porcelain cylinders as standards), we feel that the value of this sort of plot may not be restricted to carbonate rocks. If its value is found to be general, there is the considerable advantage that the data for the abscissa and ordinate can be obtained within a few days on a simple, routine basis easily handled by a technician. In other words, this research is directly translatable into simple, rapid soundness tests.

CAUSE OF DETERIORATION

If ice does not cause deterioration, then the cause of unsoundness in carbonate rocks under cooling conditions may seem at first to be incomprehensible. However, if relative thermal expansion of the components in the system and the well-known ordering of water on clays are considered, a cause can be postulated for the frost deterioration.

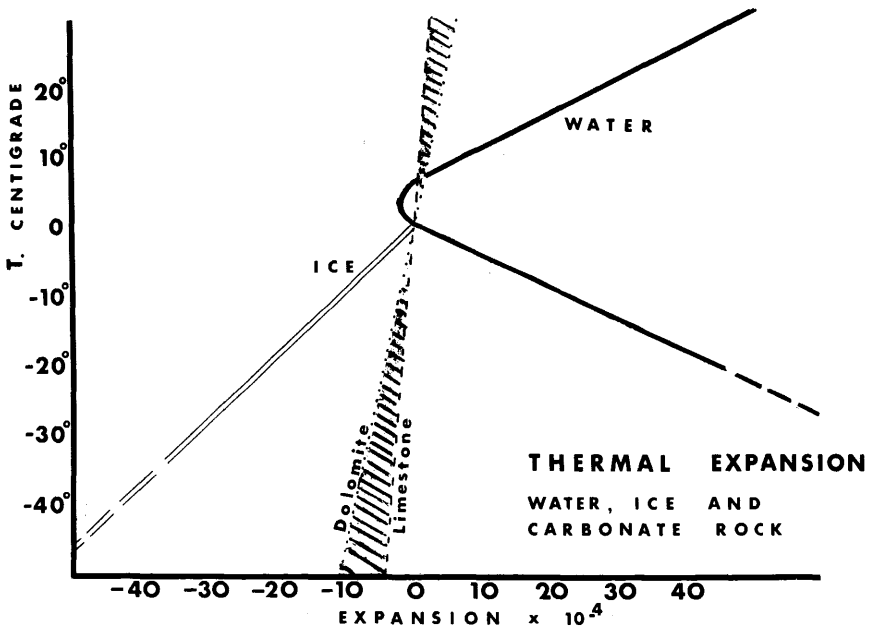


FIGURE 10. Volume per cent thermal expansion.

Figure 10 interrelates the cubical thermal expansion of water, carbonate rock, and ice at low temperatures. Note that, as ice cools below 0° C, it contracts at a far greater rate than the carbonate rocks. Unless more water is added, the ice can exert no further pressure after its initial freezing. In contrast, however, water expands rapidly on cooling below 3.98° C. Thus, if this water for any reason is not free to move, it may be capable of exerting potentially disruptive

forces. Clay mineralogists are in general agreement that water on clay surfaces (as well as on other substances) is highly ordered and rigid. Such water is not very mobile, and if it is already under pressure, cooling may expand it still further and cause disruptive forces.

The possibility of water alone causing strong internal forces is not too surprising when we recall that several of the frost-sensitive carbonate rocks in our research were disrupted merely by wetting and drying alternately. Cooling would seem to increase the forces involved.

The research results described here are in agreement with a conclusion of Bisque and Lemish (1959), that frost sensitivity in carbonate rocks is not related to pore size alone, but also to dolomite and insoluble-residue content. It is also wholly in agreement with the concept presented by Loughlin in 1923: *If these minerals* [clays] *are thinly and uniformly distributed throughout an impervious rock, air and water may not reach them to an appreciable degree, but if they are concentrated in bunches or layers, rapid disintegration is to be expected.* In other words, he stressed the need for clay to be not only present, but accessible to the elements. Our basic premise is that the action of dolomite replacing calcite in a rock is an agent of concentration for clay.

In a sense, the diagram of air-filled space after 24-hour soaking, on the abscissa, against percent of non-freezable water, on the ordinate (fig. 9), is primarily a plot of pore influence versus mineralogic influence, i.e., the ordinate is concerned with the critical saturation concept and the abscissa is concerned largely with the influence of mineral surfaces. This presents a situation which both we and Lemish, among others, have long insisted be considered: that the explanation of rock soundness is to be found in properly relating mineralogic and pore size considerations.

SUMMARY

The unsoundness of carbonate rocks, described as "frost-sensitive," appears from our research to be related not to ice but to water—ordered, expanding water. As a result of the research, this water is believed to be associated with clays rejected by dolomite. If the conclusions drawn from this research can be verified by other workers, the nature of evaluating and testing aggregate materials will be radically altered.

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